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Oxidative degradation of amine solvents for CO_2 capture

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Abstract

The oxidative degradation of diamines was measured in a stirred reactor at 70 ℃, 98kPa O_2, and 2kPa CO_2. Amines studied include ethylenediamine (EDA), propylenediamine (PDA), 1,4-diaminobutane (putrescine), hexamethylenediamine (HMDA), propanolamine (MPA), Diglycolamine® (DGA®), and bisaminoethyl ether (Jeffamine EDR-104®). Amine solutions with an initial concentration of 10 m alkalinity, an initial loading of 0.4 mol CO_2/mol alkalinity, and an initial metals concentration of 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, and 0.05 mM Cr were oxidatively degraded. The purpose of these experiments was to study the structural effect of diamines on their degradation rates.

At high metals concentration of 4 mM Fe, 2 mM Mn, 1 mM Ni, and 0.5 mM Cr, PDA does not show signs of significant degradation. This is also true for PDA at the normal metal concentration of 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, and 0.05 mM Cr. PDA was tested with antifoam and it did not show measurable degradation. EDA degradation follows zeroth order kinetics with a rate constant of 9.79 mmol/kg-hr and is likely mass transfer controlled. Putrescine degradation follows first order kinetics with a rate constant of 0.00104 1/hr and is likely kinetically controlled at experimental conditions. The degradation of HMDA follows first order kinetics with rate constant k = 0.01/hr. The degradation of bisaminoethyl ether follows first order kinetics with rate constant k = 0.023/hr. DGA® degradation also follows first order kinetics with rate constant k = 0.008/hr. HMDA, Jeffamine EDR-104®, and DGA® degradation are all kinetically controlled. MPA showed negligible degradation after 260 hours of run time. There was no significant degradation observed for PDA with normal and high metals concentration in previous experiments.

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Keywords: Oxidative Degradation; Amines

1. Introduction

Oxidative degradation of amine solvent is a major source of solvent loss in flue gas carbon capture and mainly occurs in the absorber. The products of oxidative degradation have yet to be completely identified, and it is important to understand degradation mechanisms and the environmental impact of degradation products.

Previous studies on oxidative degradation by Voice, Goff, Zhou and Sexton focused on MEA degradation, oxygen mass transfer, and catalysts [1-4]. They found that Fe (II or III) and Cu (I) are potent catalysts, as are Mn and Cr. Voice found Ni to have no effect on oxidation while Sexton classifies it as a catalyst. They also screened amines for their degradation behaviors at absorber condition—putrescine, hexamethylenediamine (HMDA), and monopropanolamine (MPA) are resistant to oxidation while ethylenediamine (EDA), Jeffamine EDR-104®, and diglycolamine® (DGA®) are susceptible to oxidation. Voice concluded that tertiary amines, rings, hindered amines and those with no alpha hydrogen are likely to resist oxidation.

Following previous work, this study focuses on screening amines based on their structure and looking for correlation between amine structure and oxidative degradation behavior.

2. Experimental Methods

Solutions were prepared gravimetrically. The target amine concentration was 10 m alkalinity and the target CO_2 loading was 0.4 mol CO_2/mol alkalinity.

A schematic of the low gas flow apparatus is shown below. The apparatus is identical to the LGF reactor used by Voice [1] and approximates conditions in the absorber. Carbon dioxide and oxygen were passed through two calibrated mass flow controllers to maintain a reactor pressure of 98 kPa O_2 and 2 kPa CO_2, and the jacketed glass reactor was charged with approximately 350 ml of amine solution. The reactor head was sealed with a Teflon® cap. The O_2/CO_2 mixture was saturated with water before being fed to the reactor through the Teflon® cap. The reactor was agitated at 1400 rpm and maintained at 70 ℃.

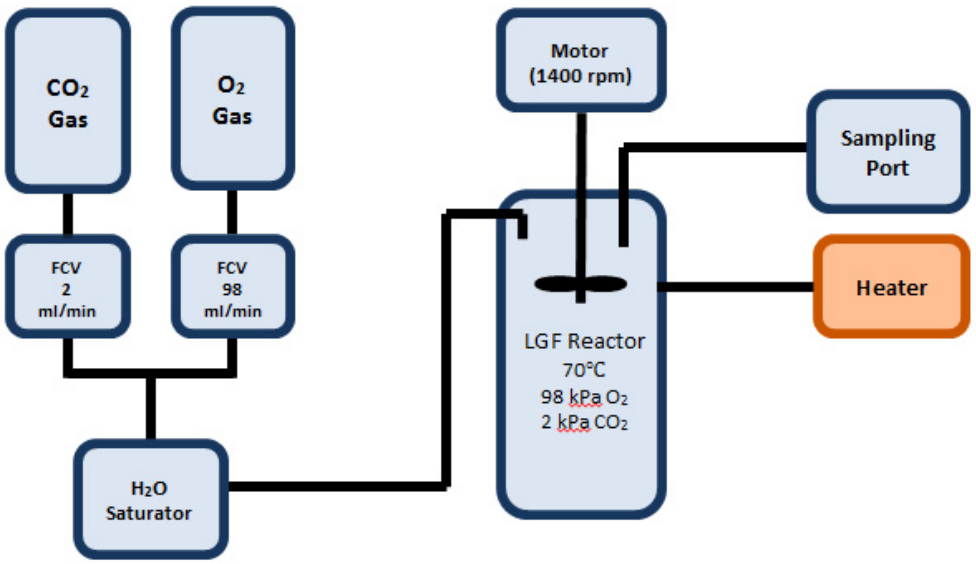


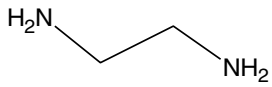
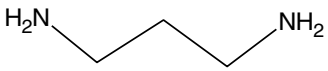
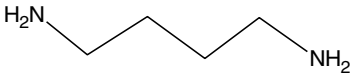
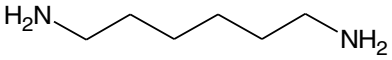
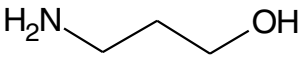
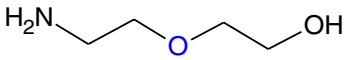
Fig. 1. Low gas flow oxidation apparatus

The water balance was maintained by adding water each time a sample was removed to make up for water loss through evaporation. Table 1 lists a sampling schedule that was generally followed for each experiment. The amines tested in this study included 1,4-diaminobutane (putrescine), ethylenediamine (EDA), 1,3-diaminopropane (PDA), hexamethylenediamine (HMDA), propanolamine (MPA), Diglycolamine® (DGA®), and bisaminoethyl ether (Jeffamine EDR-104®). The structures of these amines are listed in Table 2.

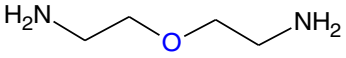
Table 1. General sampling schedule of oxidation experiments

Sample number	Time since start of experiment
1	At starting time
2	1 day
3	2 day
4	3 days
5	4 to 5 days
6	6 to 7 days
7	9 to 10 days
8	13 to 14 days

Table 2. Diamines tested in the LGF

Amine Name	Abbreviation	Structure
Ethylenediamine	EDA	
1,3-diaminopropane	PDA	
1,4-diaminobutane	Putrescine	
Hexamethylenediamine	HMDA	
Propanolamine	MPA	
Diglycolamine®	DGA®	

Bisaminoethyl ether Jeffamine EDR-104®



Cation chromatography was used to analyze for parent amine concentrations and degradation by-product concentrations; samples were diluted by a factor of 10000, and the separation was carried out using a Dionex CS17 column. Anion chromatography was used to qualitatively analyze for formate salts and nitrite. Samples were first hydrolyzed using concentrated sodium hydroxide and then diluted by a factor of 100. The separation was carried out using a Dionex AS15 column. The analytical methods are identical to those of Voice [1].

3. Results

Figure 2 shows the degradation of PDA with high and low metals. The amine concentrations are calculated based on cation chromatography results. PDA does not show significant degradation and the fluctuations are likely noise caused by water balance adjustments. A considerable amount of foam formed at the gas-liquid interface in both experiments. As a result, PDA was tested again with antifoam to study whether foaming on the solution surface is hindering oxygen diffusion into the bulk solution and hindering oxidation. Approximately 1 ml of antifoam was added to the PDA solution together with the metals at the start of the experiment, and as data in Figure 2 show, antifoam did not alter the degradation behavior of PDA.

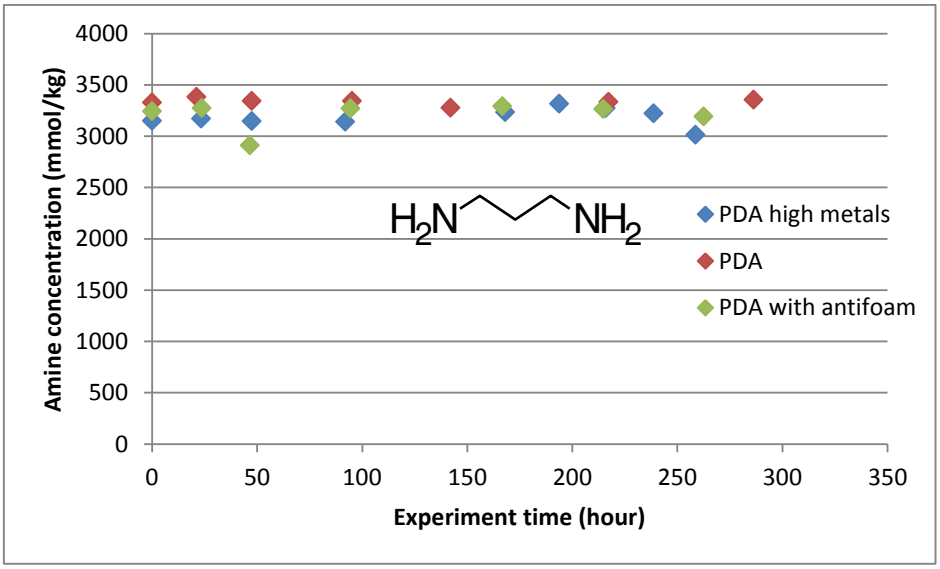


Figure 2. Oxidation of 5 m PDA. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

The concentration of heat stable salts for PDA with antifoam is shown in Figure 3. The concentration is almost zero, indicating that almost no oxidative degradation took place.

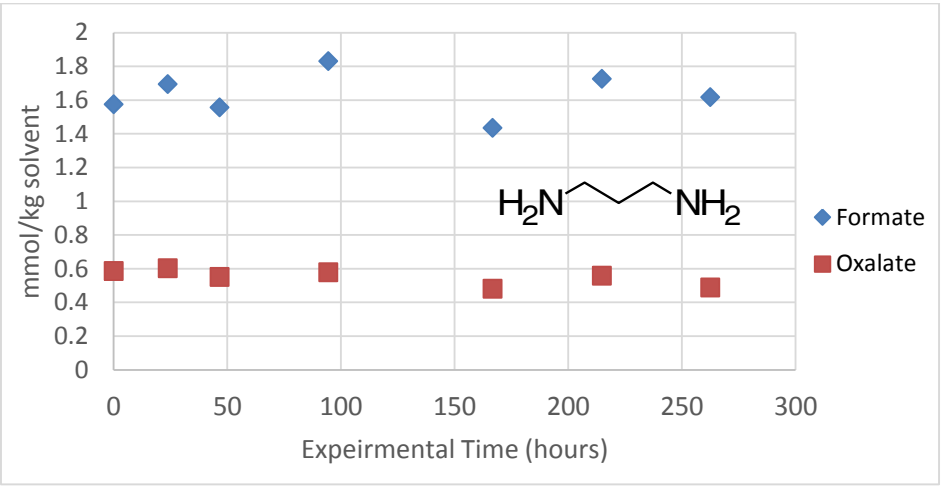


Figure 3. Total formate and total oxalate in oxidation of 5 m PDA. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

The degradation of EDA follows zeroth order behavior with a rate constant of 9.79 mmol/kg-hr while degradation of putrescine follows first order behavior with a rate constant of 0.0104 1/hr. These data are summarized in Figures 4 and 5.

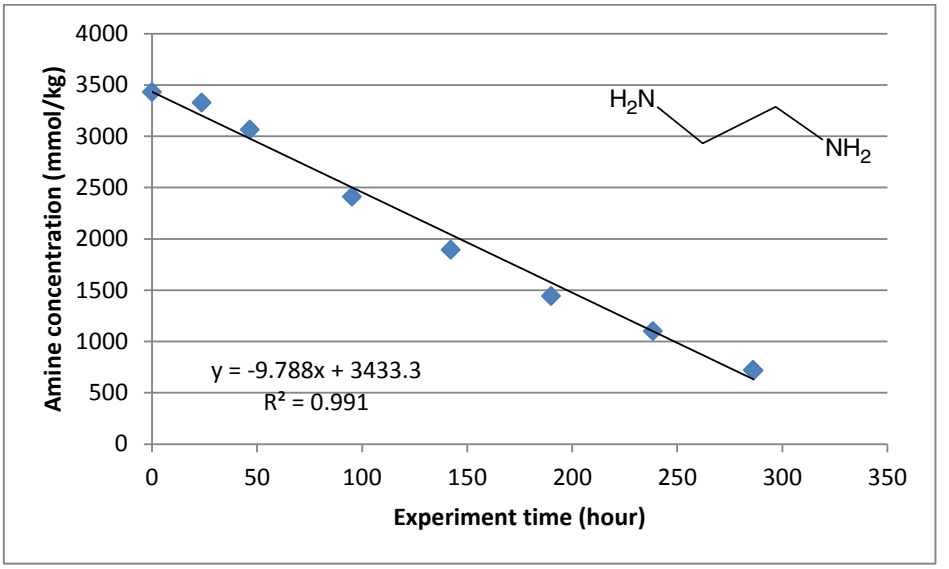


Figure 4. Oxidation of 5 m EDA. Conditions: 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm, 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, 0.05 mM Cr.

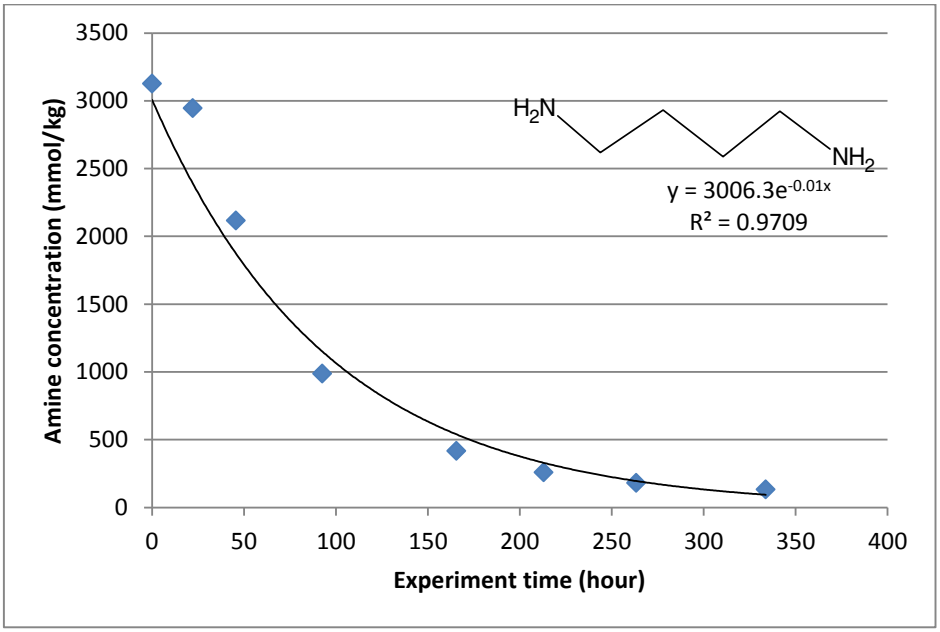


Figure 5. Oxidation of 5 m putrescine. Conditions: 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm , 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, 0.05 mM Cr.

Based on the degradation rates of EDA and putrescine, EDA degradation is likely mass transfer controlled or catalytically controlled while putrescine degradation is likely kinetically controlled. Putrescine degradation seems to approach an equilibrium once 90% of the original solvent degraded after approximately 220 hours. These results disagree with Voice in that putrescine is resistant to oxidation, but agree with his observation that EDA is susceptible to oxidation. Voice observed that iron suppressed EDA oxidation, which produced volatile products.

Figure 6 shows the degradation of putrescine. Putrescine seems to undergo a short induction stage where degradation is very slow at first but then rapidly accelerates. Degradation of putrescine is kinetically controlled and follows first order kinetics with rate constant k = 0.01/hr. About 96% of the initial amount of amine was lost to degradation.

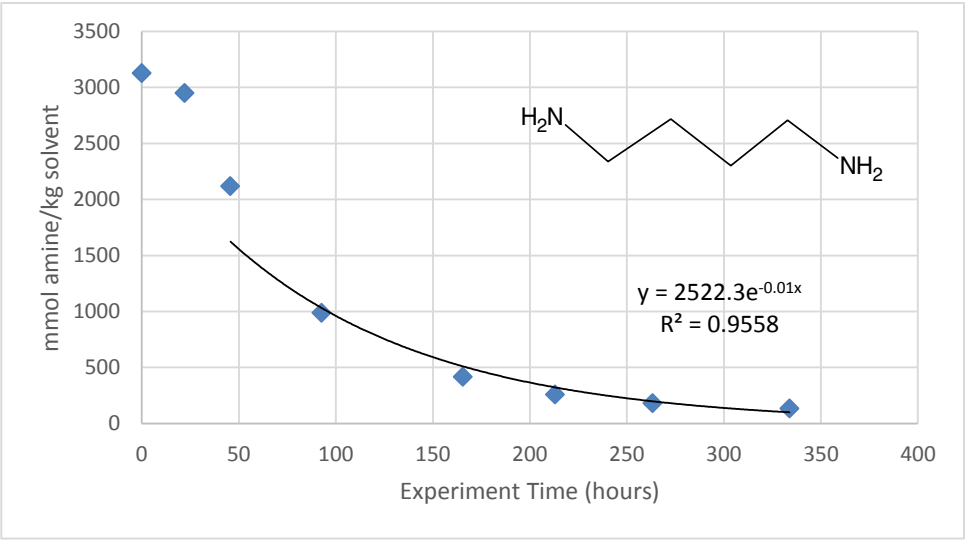


Figure 6. Oxidation of 5 m putrescine. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Anion chromatography data of heat stable salt products formed from putrescine oxidation are shown in Figure 7. The ratio of formate heat stable salts to oxalate heat stable salts is about 3:1.

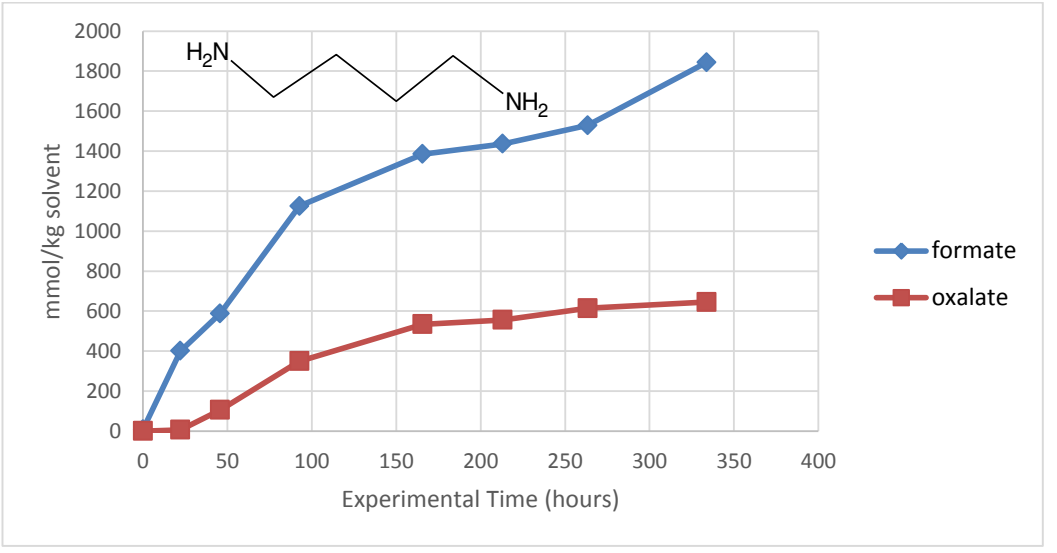


Figure 7. Total formate and total oxalate in oxidation of 5 m putrescine. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figure 8 shows the degradation of HMDA. An induction period similar to that in putrescine is observed, so only the last four data points were used to calculate the rate of degradation. HMDA shows degradation that is kinetically controlled following first order reaction kinetics with rate constant k = 0.01/hr. About 80% of the initial amount of amine was lost to degradation.

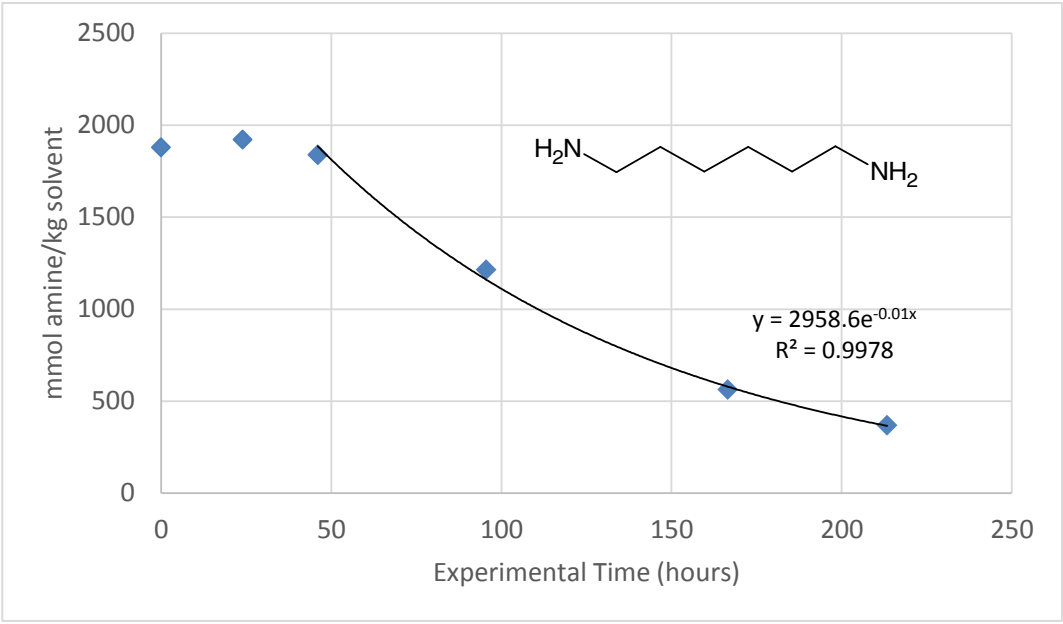


Figure 8. Oxidation of HMDA. 70℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figure 9 shows the heat stable salts produced from oxidation of HMDA. Formate forms at a slightly greater rate than oxalate, and the amount of heat stable salts formed is much less than from putrescine. The general trend for heat stable salt formation agrees with the rate of amine loss in Figure 7.

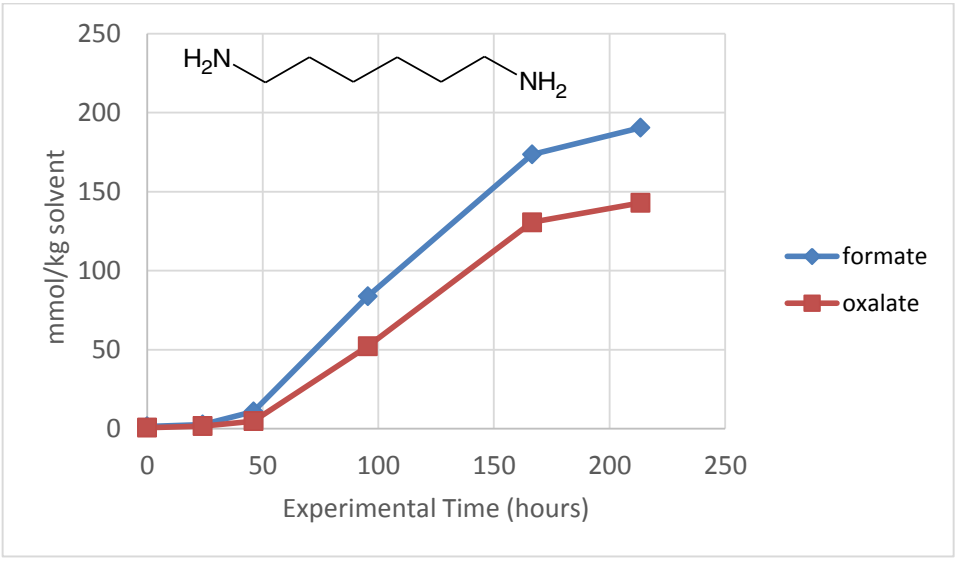


Figure 9. Total formate and total oxalate of HMDA. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figure 10 shows the degradation of Jeffamine EDR-104®. There is no observable induction stage for this amine, but the degradation is still kinetically controlled following first order reaction kinetics with rate constant k = 0.023/hr. The rate constant is much higher than that of the other amines tested. About 90% of the initial amount of amine was lost to degradation.

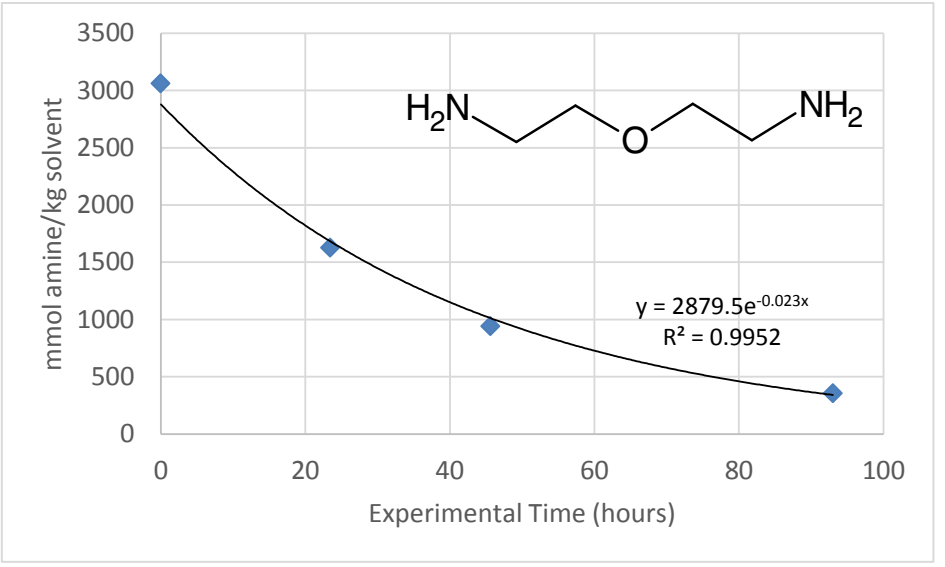


Figure 10. Oxidation of Jeffamine EDR-104®. 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figure 11 shows the formate from oxidation of Jeffamine EDR-104®. Oxalate was detected but could not be quantified.

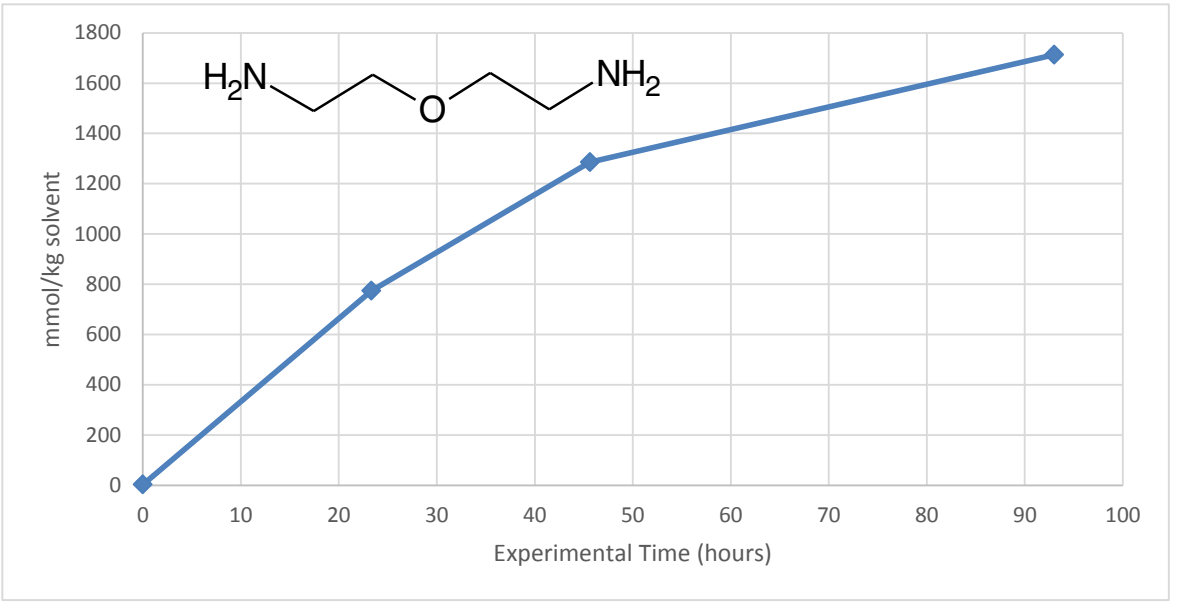


Figure 11. Total formate of Jeffamine EDR-104®. Conditions: 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figures 12 shows the degradation of DGA®. There is no observable induction stage for this amine, but the degradation is still kinetically controlled following first order reaction kinetics with rate constant k = 0.008/hr. About 80% of the initial amount of amine was lost to degradation.

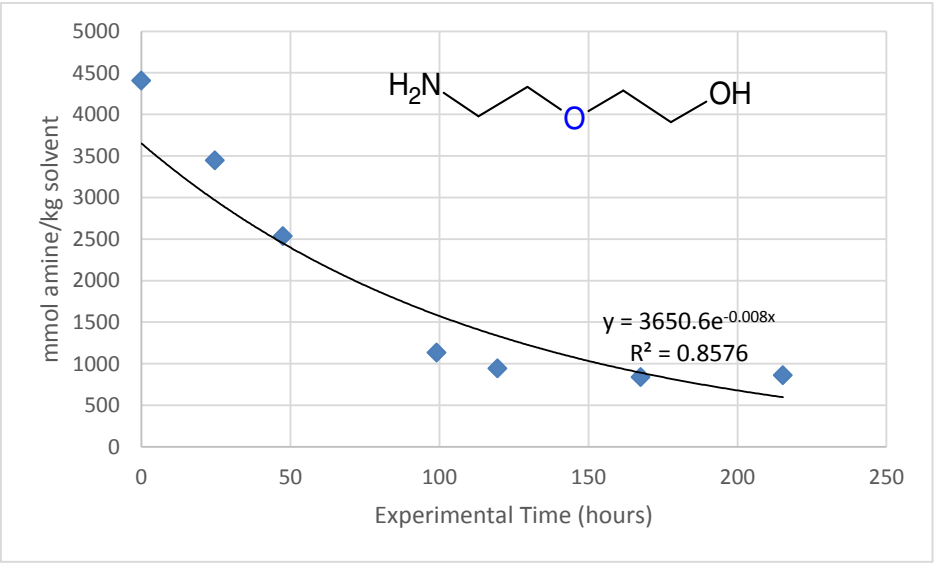


Figure 12. Oxidation of DGA®. Conditions: 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

Figure 13 shows the degradation of MPA. This amine showed negligible degradation with a 10% amine loss over 260 hours.

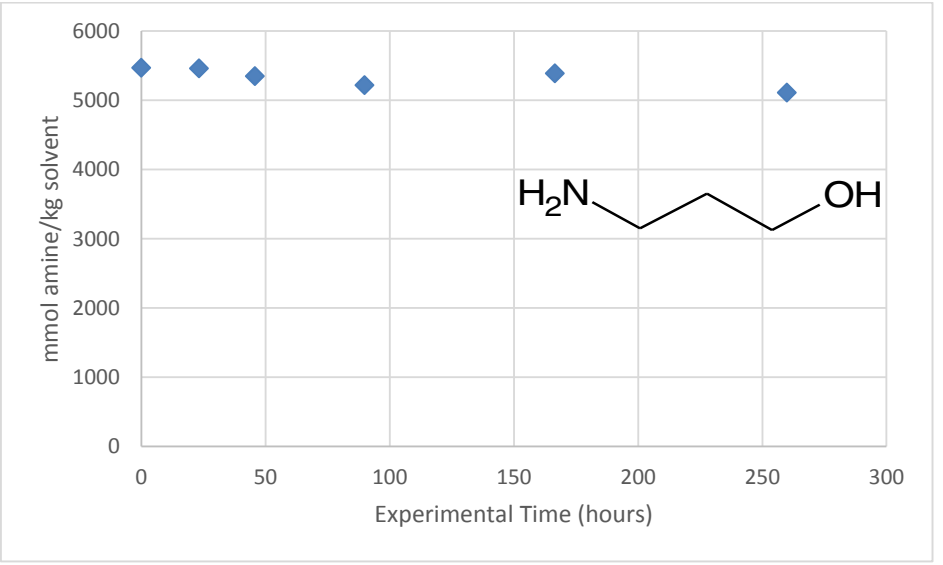


Figure 13. Oxidation of MPA. Conditions: 70 ℃, 98 kPa O_2, 2 kPa CO_2, 100 ml/min gas flow, 1400 rpm.

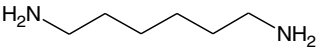
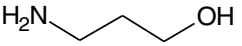
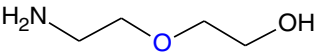
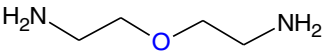
The amines that showed significant degradation all have even numbers of carbon atoms in their chains. MPA and PDA both contain three carbons in their alkyl chain and both showed negligible degradation. Catalysts form a homogenous solution with the amine samples that degraded significantly, but settled out of solution in the case of MPA and PDA. Data from thermal degradation of PDA showed that PDA and its thermal degradation products are not corrosive, further suggesting that metals likely did not catalyze oxidative degradation due to their insolubility in MPA and PDA [5]. An induction stage was observed in many amines that showed significant degradation. The

initial degradation products may have dissolved the added metals, which subsequently catalyzed degradation and caused rapid amine loss.

4. Conclusions

The table below summarizes experimental observations. A detailed list summarizing degradation behavior of the amines tested follows.

Table 3. Degradation behavior of amines at 70 ℃, 98 kPa O_2, 2 kPa CO_2 , 1400 rpm, 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, and 0.05 mM Cr

Amine Name	Abbreviation	Structure	Rate	Reaction order	Control Mechanism
Ethylenediamine	EDA		k=9.8 mmol/kg*hr	Zeroth order	Mass Transfer Controlled, could be strongly catalyzed
1,3-diaminopropane	PDA		No significant degradation, metal insolubility observed		
1,4-diaminobutane	Putrescine		k=0.01/hr	First order	Kinetically/Catalytically Controlled
Hexamethylenediamine	HMDA		k=0.01/hr	First order	Kinetically/Catalytically Controlled
Propanolamine	MPA		No significant degradation, metal insolubility observed		
Diglycolamine®	DGA®		k=0.008/hr	First order	Kinetically/Catalytically Controlled
Bisaminoethyl ether	Jeffamine EDR-104®		k=0.023/hr	First order	Kinetically/Catalytically Controlled

All of these conclusions were developed at at 70 ℃, 98 kPa O_2, 2 kPa CO_2 with 0.4 mM Fe, 0.2 mM Mn, 0.1 mM Ni, and 0.05 mM Cr.

1. PDA does not show appreciable oxidation with or without antifoam. This shows that foaming is not the reason for PDA resistance to oxidative degradation and experimental observations suggest that metal insolubility may be the cause.
2. EDA oxidizes at 9.8 mmol/kg*h. EDA degradation follows 0th order kinetics and is either mass transfer controlled or strongly catalyzed by the presence of metals.
3. MPA does not show appreciable oxidation. Experimental observations suggest that metal insolubility may cause MPA to be resistant to oxidative degradation.

4. Putrescine oxidizes at 0.01/hr. Putrescine degradation follows first order kinetics and is strongly catalyzed by the presence of metals. Degradation of putrescine produces formate and oxalate at a concentration ratio of approximately 3:1.
5. HMDA oxidizes at 0.01/hr. HMDA degradation follows first order kinetics and appears to be kinetically controlled. Degradation produces about the same amount of formate and oxalate.
6. Bisaminoethyl ether (Jeffamine EDR-104®) oxidizes at 0.023/ r. Its degradation follows first order kinetics and appears to be kinetically controlled.
7. DGA® oxidizes at 0.008/hr. DGA® degradation follows first order kinetics and appears to be kinetically controlled.
8. Amines with three carbons separating the two amino groups (PDA) or the amino group from the hydroxyl group (MPA) seem to be less susceptible to oxidation compared to amines with an even number of carbons separating the amino group from the neighboring functional group.

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The authors declare the following competing financial interest(s): One author of this publication consults for Southern Company and for Neumann Systems Group on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by the University of Texas at Austin in accordance with its policy on objectivity in research. The authors have financial interests in intellectual property owned by the University of Texas that includes ideas reported in this paper.

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